Structure and Absolute Configuration of Oplopanone, from *Oplopanax japonicus* (NAKAI) NAKAI

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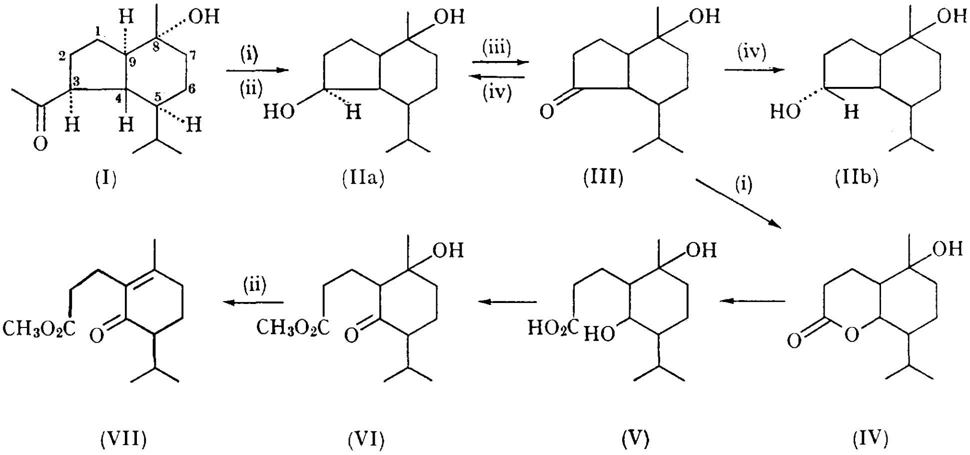
A NEW sesquiterpenic ketone, oplopanone (I), $C_{15}H_{26}O$, m.p. 96—97°, $[\alpha]_D$ −20·0°, was isolated from the whole plant of *Oplopanax japonicus* (NAKAI) NAKAI. An alcohol (IIa) was obtained by trifluoroperacetic acid oxidation of (I) followed by hydrolysis. Oxidation of (IIa) (chromium trioxide) afforded a five-membered ring ketone (III) ($\nu_{max.}$ 1730 cm.$^{-1}$), which was reduced with lithium aluminum hydride to give (IIa) and a small amount of its isomer (IIb). The ketone (III) under further oxidation (trifluoroperacetic acid) afforded a δ-lactone (IV) ($\nu_{max.}$ 1727 cm.$^{-1}$). The corresponding hydroxy-acid (V) was converted into a keto-ester (VI) by chromium trioxide oxidation followed by treatment with diazomethane. The keto-ester (VI) was dehydrated with potassium carbonate to give an αβ-unsaturated ketone (VII) [$\lambda_{max.}$ 245 mμ (ε 10,200), $\nu_{max.}$ 1670 and 1637 cm.$^{-1}$] which shows signals for a methyl on a double bond (τ 8·04) and an isopropyl group (τ 9·10) but no vinyl protons in the n.mr. spectrum.



(i) O (ii) OH$^-$ (iii) CrO_3 (iv) $LiAlH_4$

From these results and the biogenesis of the sesquiterpene, it is reasonable to suppose that oplopanone (I) may belong to the modified cadinane-type sesquiterpenes.

Oplopanone (I) was reduced with lithium aluminum hydride to the corresponding alcohol (VIII), the methanesulphonate of which was heated in pyridine to afford the unsaturated compounds (IX and X). Compound (IX) was oxidized with osmium tetroxide to give isomeric trihydroxy-compounds (XIa and XIb). Treatment of (XIa or XIb) with methanesulphonyl chloride in pyridine afforded the ketone (XII) or (XIII), respectively, and the former was quantitatively isomerized to the latter by treatment with 1% sodium hydroxide in methanol. When (XII) was dehydrogenated (10% palladium–charcoal), 8-isopropyl-2,5-dimethyl-1-naphthol (XIV)[1] was obtained. Moreover, as (XIII) was identical with the compound* synthesized by Herout and Sykora[2] the structure of oplopanone was established to be formula (I).

Since, ketone (XIII) was obtained from α-cadinol (XV),[2] the stereochemistry of oplopanone was therefore elucidated, except for the configuration at C-3 and C-4. As an optical rotatory dispersion study of (III) shows a positive Cotton effect[3] ($a = +179$), the hydrogen at C-4 should be β-oriented in oplopanone. Application of the benzoate rule[4] to (IIa) or (IIb) indicates that the hydroxyl group at C-3 in (IIa) is β-oriented and in (IIb) is α-oriented as shown in the Table.

	$[M]_D$ of benzoate	$[M]_D$ of alcohol	$\Delta[M]_D$
(IIa)	+238	−28	+266
(IIb)	−282	−147	−135

Therefore, the absolute configuration of oplopanone must be represented by (I).

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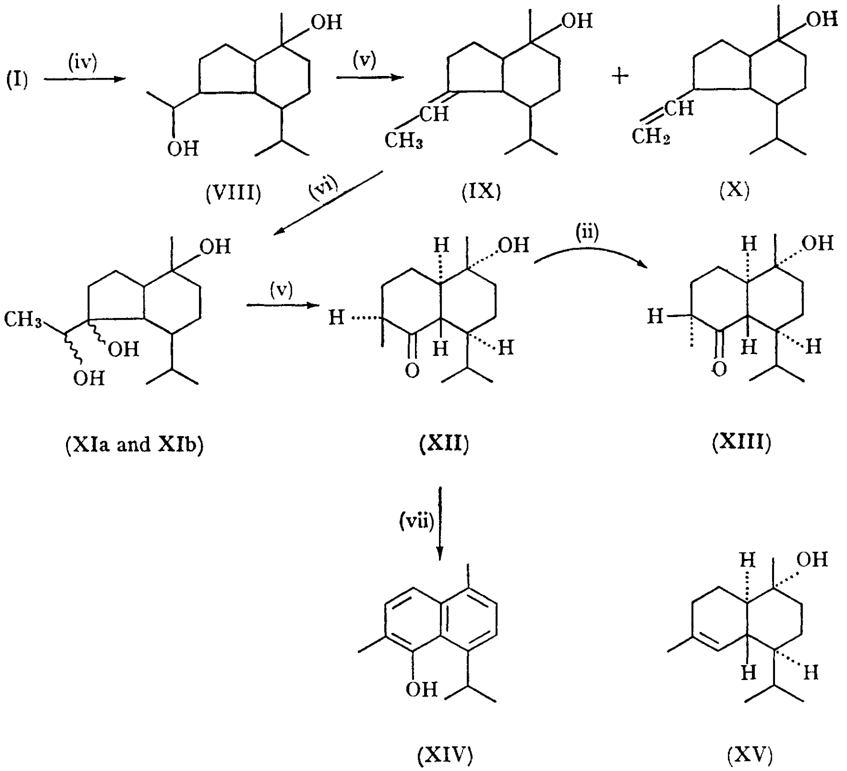
[1] K. Takeda, H. Minato, and S. Nosaka, *Tetrahedron*, 1961, **13**, 308.

[2] V. Herout and V. Sykora, *Tetrahedron*, 1958, **4**, 246.

[3] W. Klyne, *Tetrahedron*, 1961, **13**, 29.

[4] J. H. Brewster, *Tetrahedron*, 1961, **13**, 106.



(v) MsCl/pyridine (vi) OsO_4 (vii) $-H_2$

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